Enhanced performance of spherical natural graphite coated by $Li_4Ti_5O_{12}$ as anode for lithium-ion batteries

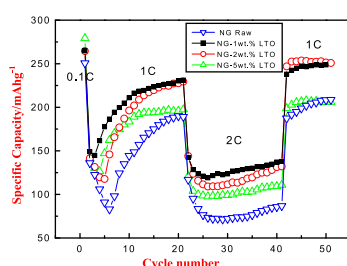Mi Lu [a,*], Yanyan Tian [b], Xiaodong Zheng [a], Jun Gao [b], Bing Huang [a]

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HIGHLIGHTS

► A new kind of coating material, $Li_4Ti_5O_{12}$, was introduced onto the surface of natural graphite.
► The energy and power densities, cycle life and safety performance of natural graphite are enhanced by $Li_4Ti_5O_{12}$ coating.
► In situ formed lithiated LTO with higher electronic conductivity in the final coating material on the graphite.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

The natural graphite (NG) is coated with $Li_4Ti_5O_{12}$ (LTO) and the composite shows a markedly enhanced rate performance due to the decrease of charge transfer resistance after LTO coating. The specific capacity of the NG charge-discharged at 2 C is increased by 60.3% (128.7 vs. 80.3 mAh g^{-1}) by coating it with 1 wt.% of $Li_4Ti_5O_{12}$ (LTO). The comparison of the NG and that coated with 1 wt.% LTO at 0.1 C shows that the initial reversible capacity is increased from 318.1 mAh g^{-1} to 357.5 mAh g^{-1} after coating, while the total irreversible capacity loss after 50 cycles is decreased from 122.8 mAh g^{-1} to 103.9 mAh g^{-1}. The composite improves the energy and power densities, safety, cycle life and lowers the price of the lithium-ion battery while avoiding the gas-swelling of full battery caused by Ti^{4+} because the final coating material is the lithiated LTO ($Li_7Ti_5O_{12}$ or $Li_9Ti_5O_{12}$).

1. Introduction

The issues that the lithium-ion batteries used in electric vehicles include safety, cost, cycle life, energy and power densities [1]. Its cost is mainly determined by the price of the raw material. Natural graphite (NG) possesses the advantages of abundance, low price and high specific capacity and has attracted significant attention as a potential anode material for lithium-ion batteries [2,3]. However, NG anode has exhibited some disadvantages such as low initial coulombic efficiency, poor cycle and rate performance. Two defects above may be overcome by oxidation [4,5], sulfuration [6], or surface coating. The coated materials include carbon [7–10], polymer [11], alkali carbonate [12], and lithium benzoate [13]. But its rate performance was little improved by those methods. Even much new material systems were investigated, it is generally accepted that graphite electrodes will remain the most important and relevant anodes in Li-ion batteries for electric vehicles application [14], thus how to keep its advantages while improving its disadvantages, especially rate performance, is a big challenge. The NG shows a much high electronic conductivity of $0.4–2.5 \times 10^4$ S cm^{-1} at its basal plane (graphene layer) but much lower value of 1–5 S cm^{-1} alone c direction (edge plane), with 5000 folds lower than that at

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the basal plane [15]. The diffusivity of lithium ion within carbonaceous materials is also high ($\sim 10^{-8}$ cm^2 s^{-1}), thus its rate performance is determined by the interfacial charge transfer reaction [16]. Surface coating is a mature technology that forms a core−shell structure, combining the advantages of the core and shell materials. Li$_4$Ti$_5$O$_{12}$ shows a much higher fast charge/discharge performance when its electronic conductivity is improved, and its cyclic stability and initial coulombic efficiency are also attractive [17,18], which is ideal as a coating material for NG anodes for lithium-ion batteries due to the improvement of its electronic conductivity.

2. Experimental

2.1. Sample preparation

The intended Li$_4$Ti$_5$O$_{12}$ contents are 1, 2, and 5 wt.% of the total NG−Li$_4$Ti$_5$O$_{12}$ (denoted as NG−LTO) composite. Stoichiometric amounts of tetrabutyl titanate and NG powder were added to an adequate volume of alcohol and stirred overnight, resulting in the tetrabutyl titanate to adsorb onto the surface of the NG. Then, a stoichiometric amount of lithium acetate dissolved in water was dripped into the emulsion, and the tetrabutyl titanate was hydrolyzed to form TiO$_2$. Then the solvents were evaporated by heating and stirring the slurry for some time, leaving the lithium acetate homogenously adsorbed on the surface of the NG. The mixture of graphite absorbed with TiO$_2$ and lithium acetate was heat-treated at 800 °C in the argon atmosphere for 12 h to obtain the NG−LTO composite. The NG used in this paper is a kind of spherical natural graphite made from natural flake graphite, which was supplied by BTR New Energy Materials Inc. (Shenzhen, China).

2.2. Physical characterization

The morphology of the samples was observed using a scanning electron microscope (SEM) (S4800, Hitachi, Japan) operating at 15 kV. The structure of the samples was measured by X-ray diffraction (XRD) (X'pert PRO, Panalytical, Netherlands) with CuKα radiation ($\lambda = 0.15418$ nm) within a region of 10−90°.

2.3. Electrochemical measurement

A slurry of the NG−LTO composite was prepared by ball-milling a mixture of 10 wt.% polyvinylidene fluoride (PVdF) with an adequate amount of N-methyl-2-pyrrolidone (NMP) for 2 h. The slurry was coated onto copper foil with a surface area of 1 cm^2 and then dried at 100 °C under vacuum for more than 10 h to obtain an electrode for electrochemical measurement. CR2025 coin-type cells were assembled in an argon-filled glove box (Etelux 2000, China) in which both moisture and oxygen levels were kept at less than 1 ppm. LiPF$_6$ (1 M) in ethylene carbonate and dimethyl carbonate (EC−DMC, 1:1 v/v) was used as the electrolyte and lithium foil was used as the counter electrode. The cells for rate performance tests were stored for 1 day and these for cyclic performance tests at 0.1 C were stored for 3 days to analyze the effect of the storage time on the NG anode performance. Charge/discharge cycles were performed using a Neware® instrument (China) at different C rates (1 C = 372 mA g^{-1}). Considering the effect of polarization, the cut-off potentials of discharge process at 0.1 C, 1 C and 2 C are 0.005, −0.010 and −0.020 V, respectively.

3. Results and discussion

3.1. Physical characterization

SEM images of the NG and NG−LTO composite are shown in Fig. 1. It is found that many dots are distributed on the surface of NG−LTO composites in comparison with NG, indicating that LTO has been successfully introduced onto the surface of NG. This trend becomes more apparent for the samples with 2 and 5 wt.% LTO coating, for which the coating is more homogenous. It can be seen
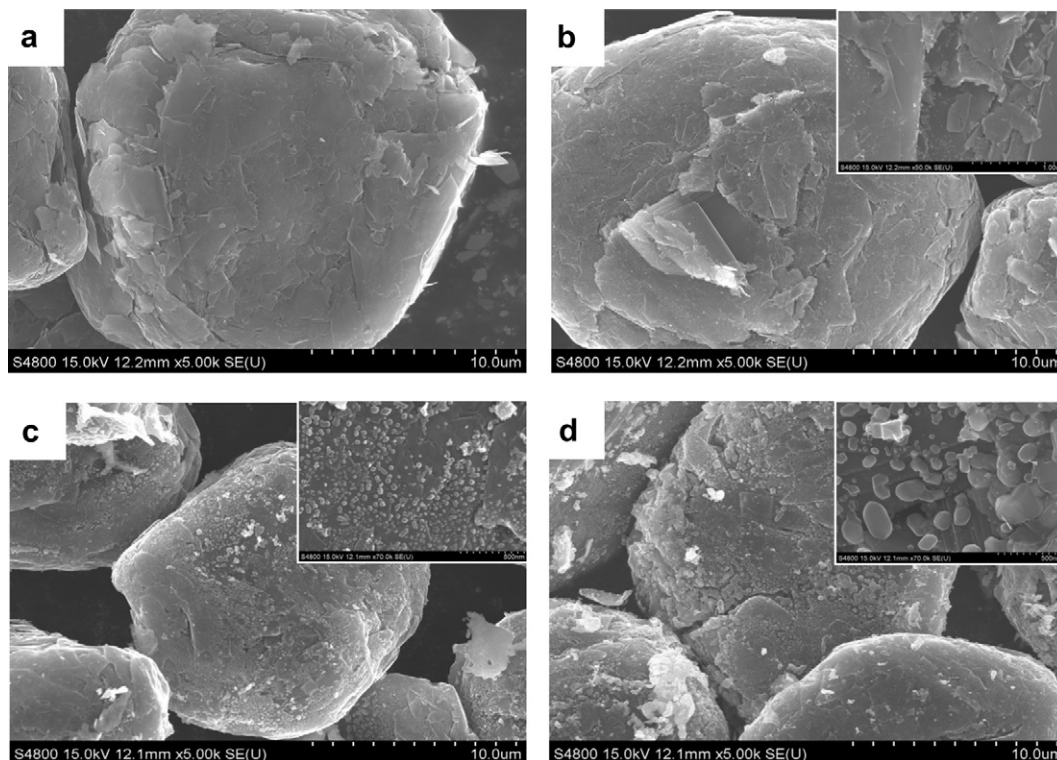

Fig. 1. Surface morphology of (a) NG, (b) NG−1 wt.% LTO, (c) NG−2 wt.% LTO, (d) NG−5 wt.% LTO.

from these SEM images that the particle size of LTO on the surface of NG increases with the increasing of the LTO contents due to the aggregation of the raw materials.

Fig. 2 presents XRD patterns of the NG and NG–LTO composites. It shows that the positions ascribed to graphite are the same, indicating that the LTO coating does not change the characteristics of graphite. Furthermore, the diffraction peaks of graphite are very sharp, reflecting that the NG has high crystallinity. By coating NG with LTO, the diffraction peak corresponding to the (111) face of LTO appears at 18.43°, and the peak intensity is enhanced with the increasing of LTO content. The particle sizes of LTO in the composites coating 1, 2 and 5 wt.% of LTO, which are calculated from Scherrer's equation, are 19.6, 67.1 and 78.3 nm, respectively. The trend is consistent with the SEM results in Fig. 1. The XRD patterns of the composites containing 2 and 5 wt.% of LTO also show some peaks corresponding to TiO_2, which may be caused by the contactless between the lithium acetate and TiO_2.

3.2. Rate performances of NG and NG–LTO composites

The fast charge–discharge performance of NG anode is closely related to the electrode density. The anode of NG–1 wt.% LTO with different weight of active material on the 1 cm^2 copper current collector is charge-discharged at 1 C and 2 C and the average reversible capacity of the 10 cycles and its result is shown in Fig. 3. It can be seen that their specific capacities decrease with the increasing of weight and current density. The parallel fitted curves for 1 C and 2 C indicate that the rate performances only relate to the properties of the material. Thus the electrodes with similar weight of active material are selected (2.70, 2.88, 2.70 and 2.88 mg for NG, NG–1 wt.% LTO, NG–2 wt.% LTO and NG–5 wt.% LTO, respectively) in here to measure the fast charge–discharge performance. The natural graphite mainly shows a hexagonal structure and lithium ions intercalate into the graphene layers through its edge plane. But the area of edge plane is much less than that of basal plane as observed from SEM shown in Fig. 1, the other transfer route for lithium ions is in fact mainly through the nano-sized holes on the basal plane [19]. Thus this kind of NG shows a much inferior fast charge performance than MCMB. Therefore, a charge–discharge cycle at 0.1 C rate is first employed to "activate" the electrodes, which is similar to the formation process in the manufacture of lithium ion batteries. The cyclic performances of the four samples with varied charge–discharge currents are shown in Fig. 4. Because
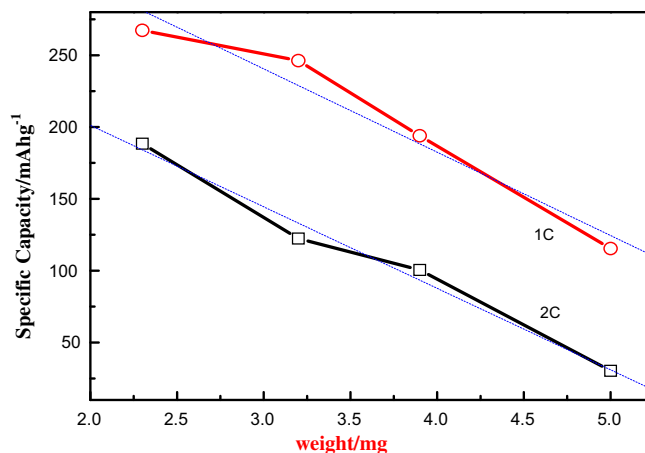
the specific capacities of the four samples during the initial cycles are unstable due to similar reason of the "active" of the electrode and their capacities are stable after 15 cycles, we discuss the fast charge–discharge performance between the 22nd and 51st cycles. The results show that the specific capacity of NG at 2 C is obviously improved by LTO coating with an optimal LTO content of 1 wt.%. When the current density is decreased to 1 C, the specific capacities of the samples containing 1 and 2 wt.% of LTO are similar, which is significantly higher than those of the samples containing 0 and 5 wt.% of LTO. The capacity of NG–5 wt.% almost equals to that of raw NG at 1 C, indicating that the too much of LTO may decrease the reversible capacity of the composite. The average specific capacities at 2 C and 1 C are summarized in Table 1. It shows that the specific capacity of NG–1 wt.% LTO at 2 C rate is 128.7 mAh g^{-1}, while that of NG is only 80.3 mAh g^{-1}, which means that the specific capacity of NG at 2 C rate is enhanced by 60.3% with only 1 wt.% LTO coating. The improvement of about 20% is also realized by coating 1–2% of LTO at 1 C current. These results clearly demonstrate that the fast charge–discharge performance is greatly improved by LTO coating.

The improved fast charge–discharge performance is ascribed to the suppress of charge transfer resistance on the electrode/electrolyte interface [20], which can be observed from the charge/discharge curves of the 32nd (the last cycle of 2 C test) and the 51st
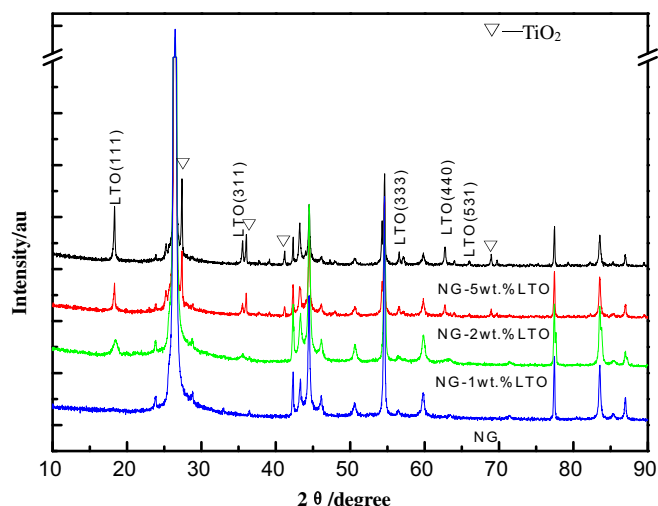
Fig. 3. The relationship between the weight of active material on the 1 cm^2 copper current collector and the specific capacity of the NG–1 wt.% LTO.
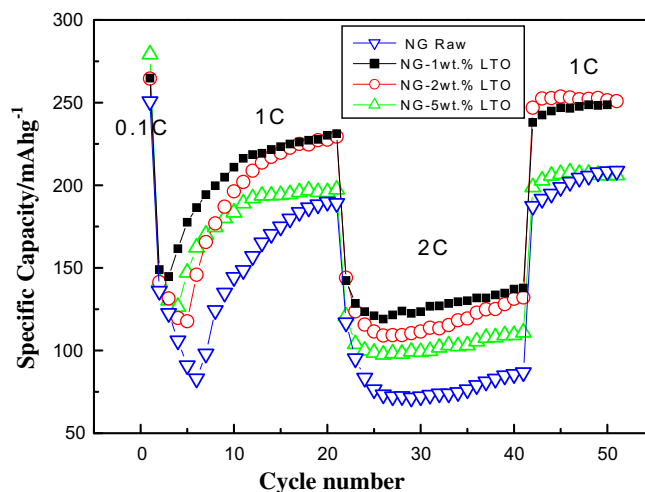
Fig. 2. XRD patterns of the four samples.

Fig. 4. The rate performances of the four samples charge-discharged at different current densities.

Table 1
The average specific capacities of the four samples charge-discharged at 1 C and 2 C calculated from the data from the 22nd to 51st cycles.

Rate	NG	NG−1 wt.% LTO	NG−2 wt.% LTO	NG−5 wt.% LTO
2 C (mAh g^{-1})	80.3	128.7	119.5	103.8
1 C (mAh g^{-1})	200.9	246.2	251.8	205.4

(the last cycle of 1 C test) shown in Fig. 5. The inflection points of the charge curves at 2 C and 1 C are at about 0.31 V and 0.24 V, respectively, indicating that the charge capacity is mainly related to the stage of graphite and the inflection point corresponding to the lithium ions is fully deintercalated from dilute stage-1 [16]. On the contrary, the discharge curve of NG at 2 C shows 22.5 mV lower than that of NG−1 wt.% LTO at the beginning of potential plateau, and enlarges to 47.6 mV at the end of discharge process of NG, indicating that the LTO coating really suppresses the interfacial charge transfer resistance of NG anode during its charging process, and the effect becomes more obviously when the more lithium ions are intercalated into the graphite layers. When the discharge current decreases to 1 C, the difference of potential between NG and NG−1 wt.% LTO decreases to 32.2 mV, indicating that more lithium ion can be intercalated into the graphite layers, thus higher charge capacity is obtained at 1 C. The reason that LTO suppresses the charge transfer resistance is attributed to the fact that the final coating material on the NG is lithiated LTO ($Li_7Ti_5O_{12}$ or $Li_9Ti_5O_{12}$) [21]. The lithiated LTO shows a higher electronic conductivity similar to metal [22], thus these lithiated LTO dots deposit on the edge plane of NG will greatly improve the charge transfer reaction alone edge plane. The cut-off potential of the measurement is rational because the cut-off voltage of lithium ion battery is higher than 2.5 V and the anode potential at this condition is lower than 1.5 V. The lithiated LTO shows the advantage of lower average valence (+3.4 for $Li_7Ti_5O_{12}$ or +3 for $Li_9Ti_5O_{12}$), which is advantage for the avoiding the gas-swelling problem caused by Ti^{4+}.

The fast charge−discharge performance discusses here without the addition of conductive carbon in the electrode, thus the improvement is only related to the NG−LTO composite itself. The improved fast charge−discharge performance shows two advantages: the less addition of high specific surface area conductive carbon (for example: the specific surface area of Super P and BP 2000 is about 60 and 1200 m^2 g^{-1}, respectively) in the electrode, resulting in higher electrode tap density and lower irreversible capacity loss; the reduced risk of explosion or fire induced by internal short circuit caused by lithium dendrite formed due to the fast charge process. The results of the rate performance measurement show that the energy and power densities, safety performance of lithium ion battery may be improved by the application of LTO coated NG anode.

3.3. Cyclic performances of NG and NG−LTO composite

To further analyze the effects of LTO coating on the cyclic performance and irreversible capacity loss of NG, the NG and NG−1 wt.% LTO composite was cycled at 0.1 C as shown in Fig. 6. The initial reversible capacity is 318.1 mAh g^{-1} for NG and increases to 357.5 mAh g^{-1} after the LTO coating. Meanwhile, the initial coulombic efficiency, defined as the delithiation capacity divided by the lithiation capacity, is enhanced from 87.3% to 88.6%. The highest capacity of the NG−1 wt.% LTO composite is 359.1 mAh g^{-1}, appearing at the second cycle, while that of NG is 337.4 mAh g^{-1}, appearing at the 14th cycle. The results show that the prolonged storage time before test may improve the initial capacity but does not change the trend. The reversible capacity of NG improves about 6.4% after LTO coating tested at 0.1 C. The reversible capacities increment of 60.3% at 2 C, 20% at 1 C, and 6.4% at 0.1 C indicate that the NG−LTO composite shows superiority to the rate performance. The improved reversible capacity at 0.1 C presents that the higher energy density may be obtained by LTO coating. The two samples
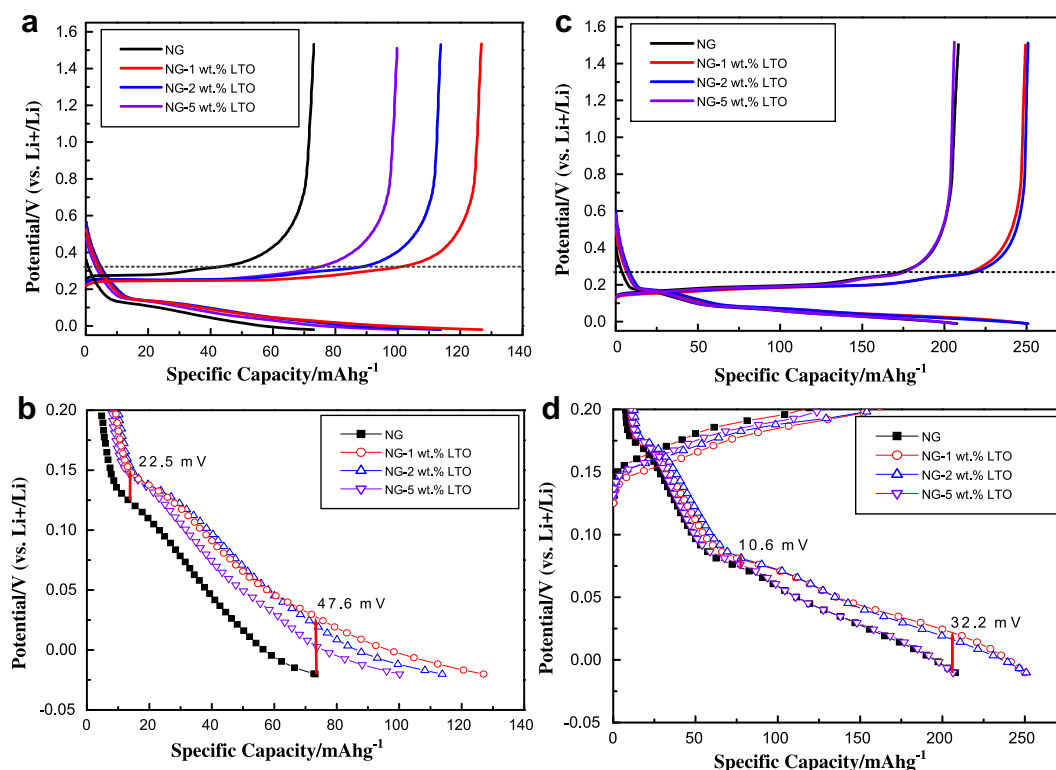

Fig. 5. The charge−discharge curves of the four samples at the 22nd and 51st cycles. (a) and (b) The 22nd cycle (2 C), (c) and (d) the 51st cycle (1 C).
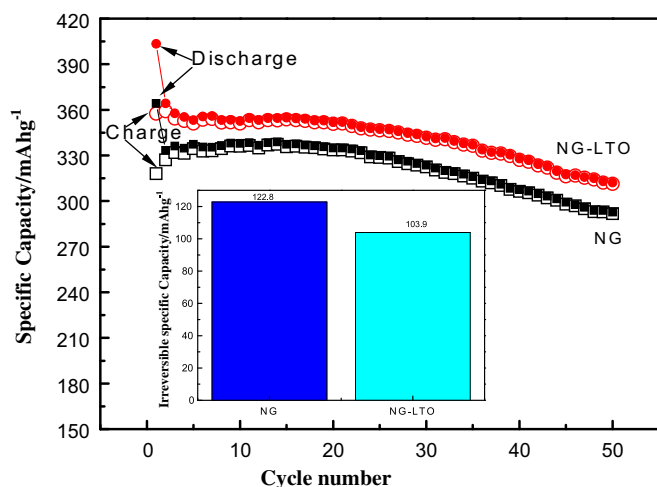
Fig. 6. The cycle performances of NG and NG–1 wt.% LTO. The total irreversible capacities of NG and NG–1wt.% LTO in the inset plot.

measured by half cell show similar capacity retention after 50 charge–discharge cycles (86.5% for NG and 86.7% for NG–1 wt.% LTO). In fact, the values of coulombic efficiency and capacity retention shown in this paper are within the error range. But the comparison of cycle life should consider that the test is done by the half-cell with abundant lithium and the cycle life is related to the irreversible capacity loss of the electrode. The total irreversible capacity loss of NG and NG–1 wt.% LTO over the 50 cycles is showed as an insett plot in Fig. 5. The values are 122.8 mAh g^{-1} for NG and 103.9 mAh g^{-1} for NG–1 wt.% LTO or the irreversible capacity loss ratios, defined as the total irreversible capacity divided by its highest reversible capacity, are 36.4% for NG and 28.7% for NG–1 wt.% LTO. The much lower irreversible capacity loss of NG–1 wt.% LTO during charge–discharge cycles indicates that the cycle life of the lithium-ion battery may be improved by application of LTO coated NG compared with that pure NG as anode for lithium-ion battery.

4. Conclusions

The fast charge–discharge performance, cyclic stability and energy and power densities, safety performance are improved by the LTO coating. The final coating material on the NG is lithiated LTO (Li$_7$Ti$_5$O$_{12}$ or Li$_9$Ti$_5$O$_{12}$), which avoids the gas-swelling problems caused by Ti^{4+} and suppresses the interfacial charge transfer resistance. The NG coats with only 1 wt.% LTO improve the capacity of at 2 C charge–discharge current by 60.3%. Results show that LTO coating is combined with the advantages but avoids the disadvantages of NG and LTO. The LTO coating is a simple, easily scaled-up method to improve the performance of NG anode.

Acknowledgments

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